Supporting Information for

Functionalized Hyperbranched Polymers via Olefin Metathesis

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Table of Contents

Materials. All reagents, except for catalyst **1** and 1-pyrenebutyric acid were purchased from Aldrich at the highest available purity and used without further purification. Catalyst **1** was obtained from Materia, Inc., and 1-pyrenebutyric acid (≥97%) was purchased from Fluka. The synthesis of **2** and its polymerization to **3** with **1** have been reported previously.[1]

Instrumentation. NMR spectra were obtained using a Varian Mercury-300 spectrometer; samples were dissolved in (methylene chloride)-d_2.

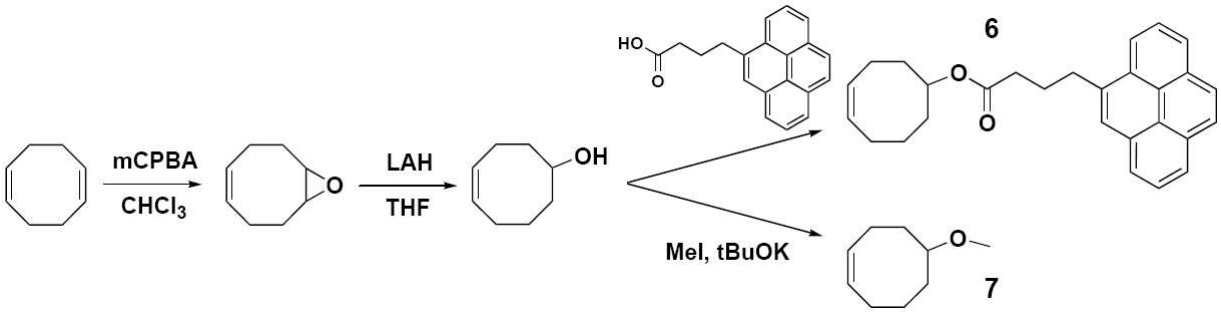
Size exclusion chromatography (SEC) analysis was performed using a Wyatt triple detector system equipped with a triple angle light scattering (miniDAWN TREOS, with a laser wavelength of 658 nm) detector, a viscometer (ViscoStar) detector, and a refractive index (Optilab rEX) detector—all operating at 25°C. Viscotek ViscoGEL I-Series (one mixed bed medium MW and one mixed bed high MW) columns were used for SEC with THF as the eluent and a Shimadzu LC-10AD pump operating at 1 mL/minute.

Fluorescence measurements were conducted using an ISS K2 fluorimeter (5 mm path length), equipped with a 250 W xenon lamp as excitation source. Emission spectra were obtained by exciting at 346 nm and monitoring the emission between 300 and 700 nm. UV-Vis spectra were recorded on a Beckman DU 7400 spectrophotometer.

Synthesis of 4-(4-pent-4-enyloxy-butyl)-pyrene (4). 1-Pyrenebutanol (1.0 g, 3.6 mmol) was combined with potassium hydride (35% suspension in mineral oil, 1.0 g, 8.7 mmol) in 10 mL of toluene in a 50 mL round bottom flask equipped with a stir bar. The suspension was stirred at room temperature until gas evolution ceased, at which point 5-bromo-pentene (0.6 mL, 5.0 mmol) was slowly added to the reaction flask. The solution was subsequently heated at reflux for 10 h. The reaction mixture was then cooled to room temperature, and the unreacted potassium hydride was neutralized with a small amount of iPrOH before the solution was filtered and concentrated under reduced pressure. The product was purified by silica gel chromatography, eluting with 5% EtOAc in hexane, and recrystallized from cold (0 °C) hexane to give a quantitative yield of pure **4** as a yellowish crystalline solid. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): 8.32 (d, J = 9 Hz, 1H), 8.19–7.97 (m, 7H), 7.90 (d, J = 7.8 Hz, 1H), 5.83 (m, 1H), 5.04–4.91 (m, 2H), 3.49–3.35 (m, 6H), 2.09 (m, 2H), 1.93 (m, 2H), 1.79–1.59 (m, 4H). ^{13}C NMR (300 MHz, CD_2Cl_2, ppm): δ 139.17, 137.80, 131.99, 131.50, 129.33, 128.04, 127.89, 127.58, 126.99, 126.37, 125.49, 125.33, 125.18, 125.04,

124.11, 114.82, 71.08, 70.66, 33.81, 30.95, 30.40, 29.62, 29.11. HRMS(FAB+) *m/z*: 342.1987 $[M]^{+\bullet}$.

Synthesis of the pyrene functionalized hyperbranched polymer (5). **3** (163 mg, 0.646 mmol in monomer), **4** (167 mg, 0.485 mmol, 0.75 equiv.), and **1** (3 mg, 3.53 μmol) were combined in 2 mL of dry CH_2Cl_2 under an inert atmosphere. The reaction mixture was stirred at 40ºC for 10 h with venting through a bubbler. Subsequently, the solution was concentrated before the product was redissolved in a small amount of CH_2Cl_2, loaded on a short silica plug, rinsed with CH_2Cl_2, and eluted with THF. The purified product was characterized by ^{1}H NMR spectroscopy and triple detector–SEC, both of which indicated clean and complete addition of **4** (~ 0.75 equivalents per repeat unit in **3**).



Synthesis of the linear pre-monomer, cycloocten-4-ol. A 250 mL round bottom flask equipped with a stir bar and an addition funnel was charged with 1,5-cyclooctadiene (8.6 g, 79.1 mmol). A solution of mCPBA (11.1 g, 64.1 mmol) in chloroform (180 mL) was added to the reaction flask drop-wise via the addition funnel. The reaction mixture was stirred for 10 h and then filtered. The filtrate was transferred to a separatory funnel and washed sequentially with saturated aqueous solutions of $NaHSO_3$ (3 times), $NaHCO_3$ (once), and NaCl (once). Purification by silica gel chromatography, eluting with 10% EtOAc in hexane, gave 4.2 g (43% yield) of the epoxide product. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 5.57 (m, 2H), 3.00–2.95 (m, 2H), 2.46–2.36 (m, 2H), 2.18–1.93 (m, 6H). ^{13}C NMR (300 MHz, CD_2Cl_2, ppm): δ 129.35, 56.95, 28.68, 24.20.

A 1 M THF solution of LAH (17.0 mL, 17.0 mmol) was slowly added via syringe to the solution of the epoxide (4.21 g, 33.9 mmol) in THF (23 mL) at room temperature and the mixture was stirred for 10 h. The reaction was then quenched with sodium sulfate decahydrate and stirred vigorously for 20 minutes. The mixture was subsequently filtered through a pad of Celite, washed

with THF, and concentrated. Purification by silica gel chromatography with a 30% EtOAc in hexane eluent afforded 4.0 g (95% yield) of a clear colorless oil. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 5.73–5.53 (m, 2H), 3.75 (m, 1H), 2.33–2.23 (m, 2H), 2.17–2.03 (m, 2H), 1.94–1.75 (m, 2H), 1.71–1.44 (m, 4H). ^{13}C NMR (300 MHz, CD_2Cl_2, ppm): δ 130.67, 129.95, 73.09, 38.29, 36.92, 26.13, 25.47, 23.30. HRMS(EI+) *m*/*z*: 126.1041 $[M]^{+\bullet}$.

(**6**). Cycloocten-4-ol (0.3 g, 2.4 mmol), 1-pyrenebutyric acid (1.0 g, 3.5 mmol), DMAP (0.6 g, 4.8 mmol), and Et_3N (1.3 mL, 9.5 mmol) were dissolved in 10 mL of dry CH_2Cl_2. 2,4,6-Trichlorobenzoyl chloride (1.16 g, 4.8 mmol) was then slowly added to the reaction mixture, and the reaction was stirred for 10 h. The unreacted benzoyl chloride was neutralized with a small amount of iPrOH before the solution was filtered and concentrated. The product was then purified by silica gel chromatography, eluting with 5% EtOAc in hexane, to give 0.9 g (95% yield) of a semi-crystalline, bright yellow material. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 8.33 (d, J = 9.6, 1H), 8.21–7.98 (m, 7H), 7.89 (d, J = 8.1, 1H), 5.76–5.60 (m, 2H), 4.86 (m, 1H), 3.38 (t, J = 7.6, 2H), 2.44–2.29 (m, 4H), 2.22–2.08 (m, 4H), 1.98–1.56 (m, 6H). ^{13}C NMR (300 MHz, CD_2Cl_2, ppm): δ 173.04, 136.77, 131.98, 131.49, 130.47, 130.34, 130.20, 129.28, 128.02, 128.00, 127.77, 127.15, 126.43, 125.54, 125.45, 125.42, 125.37, 125.28, 124.01, 76.01, 34.83, 34.33, 33.30, 28.45, 27.54, 26.14, 25.49, 22.88. HRMS(FAB+) *m*/*z*: 396.2084 $[M]^{+\bullet}$.

(**7**). Cycloocten-4-ol (0.5 g, 4.0 mmol) was combined with tBuOK (0.7 g, 6.0 mmol) in dry THF (8 mL) at room temperature. Upon addition of MeI (0.4 mL, 6.0 mmol) the reaction mixture was heated to 35 ^{o}C and stirred for 10 h. The remaining unreacted tBuOK was neutralized with a small amount of iPrOH before the solution was filtered and concentrated. Purification by silica gel chromatography, eluting with 5% EtOAc in hexane, afforded 0.15 g (27% yield) of clear colorless oil **7**. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 5.71 (m, 2H), 3.23 (s, 3H), 3.20 (m, 1H), 2.39–2.27 (m, 2H), 2.17–1.36 (m, 8H). ^{13}C NMR (300 MHz, CD_2Cl_2, ppm): δ 130.67, 129.90, 82.52, 56.15, 34.48, 33.33, 26.31, 26.20, 23.17. HRMS(EI+) *m*/*z*: 140.1201 $[M]^{+\bullet}$.

Synthesis of pyrene functionalized linear polymer (8). Monomers **6** (100 mg, 0.25 mmol) and **7** (12.0 mg, 0.08 mmol) were dissolved in dry CH_2Cl_2 (1 ml) under an argon atmosphere. Catalyst **1** (5 mg, 6 μmol) was added to the reaction flask, and the solution was stirred at 45ºC for 24 hours. Upon consumption of the monomers, the volatiles were removed under reduced pressure. The product was then redissolved in a small amount of CH_2Cl_2, loaded on a

short silica plug, rinsed with CH_2Cl_2, and eluted with THF. The purified product was characterized by ^1H NMR spectroscopy and triple detector–SEC (M_w ~ 38K, M_w/M_n ~ 1.45).